Dibenzo[\textit{b,f}]phosphepines: Novel Phosphane–Olefin Ligands for Transition Metals

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Supporting Information

ABSTRACT: New, stable heterobidentate phosphane–olefin ligands based on the dibenzo[\textit{b,f}]phosphepine backbone are reported together with their redox properties and coordination chemistry to rhodium(I). The X-ray crystal structures and DFT calculations show different conformations for the P-phenyl (6a) and P-mesityl (6b) derivatives. Cyclic voltammetry (vs Fc/Fc⁺) of 6a supported by UV–vis spectroelectrochemistry showed two cathodic waves, a reversible one at \( E_{1/2} = -2.62 \) V (Iₕ/Iₐ = 1.0) and a quasi-reversible (Iₕ/Iₐ ≈ 1.2) one at \( E_{1/2} = -3.03 \) V. Reduction with sodium afforded a mixture of the radical anion [6a]⁻, characterized by EPR spectroscopy, and dianion [6a]²⁻, for which an X-ray crystal structure was obtained. Both 6a and 6b bind to Rh¹ centers, giving rise to 3:1 (8a) and 2:1 (8b) ligand:Rh complexes, respectively. Two dibenzo[\textit{b,f}]phosphepines in 8a and 8b act as heterobidentate ligands in which both the phosphorus atom and the olefinic double bond coordinate to rhodium, but the third ligand in 8a binds as a monodentate P-donor.

INTRODUCTION

Olefin complexes of transition metals, while known for almost 200 years, remain of immense importance.¹ They are crucial intermediates in alkene modifications, where coordination of the double bond to the metal center is the first step in the catalytic transformation, as exemplified in the oxidation at palladium (Wacker oxidation), the reduction at rhodium (Wilkinson’s catalyst), and various hydrofunctionalizations (hydroamination, hydroformylation, hydrocyanation, etc.).² As auxiliary ligands, olefins steer transition-metal-catalyzed 1,4-additions and (transfer) hydrogenations.³,⁴ Especially valuable are heterobidentate ligands that contain, in addition to the olefin, an amine or phosphane donor group.⁵ Recently, a tridentate PhP(trop)₂ ligand (Scheme 1) was shown to form two unprecedented electromeric complexes with rhodium that differ substantially in their electronic structure (one isomer is the metal-centered radical [Rh⁺(L⁺)PPh₃] (1b) while the other is the ligand-centered radical [Rh⁺(L⁺)PPh₃] (1a)) but only slightly in their conformation.⁶ Phosphane–olefin ligands have further shown potential as “hydrogen reservoirs” in hydrogenation catalysis, wherein the olefin part of the ligand gets reversibly hydrogenated under the catalytic conditions, which allows hydrogen transfer to the substrate via the “cooperative ligand”. This behavior potentially leads to faster reactions and special selectivities.⁶,⁷

The noted examples point to intriguing properties associated with heterobidentate phosphane–olefin ligands and thereby call for new ones to apply in homogeneous catalysis and potentially expand the scope of electronomers. Hence, we targeted the synthesis of phosphepines 2, which differ from the known PhP(trop)₂ framework in that the phosphorus atom is embedded in the seven-membered ring (Scheme 2). The coordination chemistry of 2 is virtually unknown. We are aware

Scheme 1. Electromeric Phosphane–Olefin Complexes

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of only a single bidentate complex with iridium and a few monodentate P-coordination complexes. The underlying reason is the thermal lability of the phosphine. So far, only the parent di-tert-butyl phosphine 2a has been isolated and characterized. Less crowded phosphines (2b) are elusive, since they cyclize to unstable phosphonorcaradienes (3b) that eliminate phosphinidenes (4b). The stability of phosphines improves significantly on benzannulation, as is the case for dibenzophosphepines 6 (Scheme 3). Here we report on their synthesis, conformational analysis, (spectro)electrochemical behavior, and coordination chemistry to rhodium(I).

RESULTS AND DISCUSSION

Synthesis. Dibenzo[bf]phosphepines 6a (R = Ph) and 6b (R = Mes) were synthesized quantitatively, as monitored by 31P NMR spectroscopy, from (Z)-dibromostilbene 5 by lithiation with tert-butyl lithium and addition of the corresponding aryl dichlorophosphane at −78 °C (Scheme 3) but proved difficult to isolate due to oxidation of the phosphorus atom during chromatography. Therefore, BH3·SMe2 was added to obtain the readily purified borane complexes (yields 82% (7a), 32% (7b), 31P NMR 13.4 ppm (7a), 10.4 ppm (7b)), which on deprotection with DABCO (16 h, room temperature, DCM or toluene as solvent) afforded the desired dibenzo[bf]phosphepines 6 (yields 97% (6a), 96% (6b), 31P NMR −8.1 ppm (6a), −30.5 ppm (6b)). Crystals suitable for X-ray diffraction were obtained by slow vapor diffusion of pentane into dichloromethane solutions of 6a,b. Both molecular structures (Figure 1) have P–C bond lengths similar to those in triarylphosphines (1.82–1.84 Å for 6a and 6b vs 1.83 Å for PPh3). The sum of the bond angles around phosphorus reveals comparable pyramidalities for 6a (308.96(10)°) and 6b (312.21(15)°), as for PPh3 (309°), but the conformations differ. The phenyl group of 6a is oriented parallel to the heterocyclic double bond and has an acute dihedral angle of 60.98(9)° with the phosphine P1–C1–C14 plane, thereby rendering the phosphorus lone pair in the same spatial direction as the benzannulated rings (Figure 1, left). The molecular structure of 6b is quite different, with its mesityl group almost perpendicular to the phosphine ring and the phosphorus lone pair oriented in the direction of the vinylc bond instead of the benzannulated rings (Figure 1, right). Hence, 6b is preorganized to bind transition metals in a heterobidentate manner, while 6a has to undergo pyramidal inversion at phosphorus to bind metals in a similar manner.

The flexibility of the two dibenzo[bf]phosphepines was investigated computationally at the B3PW91/6-311G(dp) level of theory. Three different conformations I–III were identified for 6a and 6b (Figure 2; 6b lacks the mesityl's

Scheme 2. Decomposition Pathway of Phosphepines

Scheme 3. Synthesis of the Dibenzo[bf]phosphepines 6a and 6b from (Z)-Dibromostilbene 5

Figure 1. Molecular structures of 6a (left) and 6b (right) in the crystal form. Displacement ellipsoids are drawn at the 50% probability level. Selected bond lengths (Å), bond angles (deg), and torsion angles (deg) are as follows. 6a: P1–C1 = 1.8247(13), P1–C15 = 1.8373(13), C1–C6 = 1.4089(18), C7–C8 = 1.338(2), C6–C7 = 1.4669(19); C1–P1–C15 = 102.42(6), C1–P1–C14 = 102.84(6), C15–P1–C14 = 103.70(6); C16–C15–P1–C14 = 38.01(12); 6b (only one of two independent molecules is shown; hydrogen atoms are omitted for clarity): P1–C11 = 1.8348(19), P1–C15 = 1.840(2), C11–C61 = 1.411(2), C71–C81 = 1.332(3), C61–C71 = 1.468(3); C11–P1–C151 = 102.60(9), C11–P1–C141 = 105.16(8), C151–P1–C141 = 104.45(9); C161–C151–P1–C141 = −52.94(18).

Figure 2. Conformations of P-aryl dibenzo[bf]phosphanes and their relative B3PW91/6-311G(dp) energies (in kcal mol−1, ZPE corrected).
p-CH₃ group for simplicity). I resembles the molecular structure of 6a and II that of 6b, while the aryl group in III is rotated by 90° around the P−C bond as compared to the case for II. In agreement with the experimentally obtained crystal structures, I is energetically favored for the phenyl derivative 6a over II and III by 1.4 and 6.6 kcal mol⁻¹, respectively, and II is favored for 6b over I and III by +3.4 and +11.1 kcal mol⁻¹, respectively. It is evident that the o-methyl groups of the P-aryl substituent have a significant impact on the conformational stability of the dibenzo[bf]phosphepine.

While the experimentally observed conformational difference between 6a and 6b in the solid state are in agreement with the above DFT conformational analysis, we cannot exclude an additional influence of the crystal packing. In the crystal structure of 6b π−π interactions between the mesityl ring of one molecule and the aryl ring of the dibenzo(phosphepine moiety of another molecule are apparent (see Supporting Information, Figure S9).

The NMR (both 31P and 1H) spectra of 6a and 6b do not reveal the presence of different conformers, indicating a rapid equilibrium between the two major conformers I and II on the NMR time scale for both 6a and 6b (the third isomer III seems to be too high in energy to contribute significantly), which is in agreement with the low calculated barrier for I → II interconversion (~6 kcal mol⁻¹) in structurally related phosphine systems.¹¹a

**Cyclic Voltammetry and UV−Vis Spectroelectrochemistry.** To investigate the electron-accepting properties of the dibenzo[bf]phosphepine ligands, we investigated the redox behavior of 6a with cyclic voltammetry (CV). In THF 6a shows no redox activity in the potential range between −2.45 and +0.50 V (vs Fc/Fc⁺), Figure 3. At +0.55 V there is an onset of an irreversible oxidation. The CV shows a reversible cathodic wave at $E_{1/2} = −2.62$ V that forms the dibenzo(phosphepine radical anion $[6a]^-$. Scheme 4). A second wave, corresponding to the transfer of a second electron to form the phosphine dianion $[6a]^{2−}$, appears at $E_{1/2} = −3.03$ V. Measurements in commonly purified solvents and electrolyte first indicated that this wave is not fully reversible; scanning over it resulted in the appearance of a followup product showing an anodic wave at −1.76 V (marked with # in Figure 3). The two-electron-reduced phosphine apparently reacts even with traces of water in the solvent/electrolyte, leading to the redox active followup product observed with CV. More rigorous exclusion of water resulted in a fully reversible wave at −2.62 V.

We conclude that the accessibility and reversibility of both reduction waves are indicative of the electron-accepting ability of 6a, suggesting that dibenzo[bf]phosphepines can indeed be suitable π-acceptors and/or redox-noninnocent ligands in coordination chemistry.¹⁷,¹⁸

The electrochemical reduction of benzophosphine 6a in THF was also monitored by UV−vis spectroelectrochemistry using an optically transparent thin-layer electrochemical (OTTLE) cell. The spectrum shows an absorption at 304 nm (in addition to strong ones below 280 nm), which upon one-electron reduction gradually disappears with new absorptions emerging at 322, 350, 508, and 831 nm (Figure 4, left). On the basis of TD-B3LYP/def2-TZVP calculations,¹⁹ most of these bands can be assigned to stem from transitions from the SOMO to higher lying orbitals (see Table 1).

The three characteristic absorptions of $[6a]^−$ disappear in the second reduction step when a single new absorption emerges at 552 nm. This corresponds to filling the SOMO of $[6a]^−$ with an additional electron and limits the possible optical transitions for the diamagnetic, closed-shell $[6a]^{2−}$. Its TD-DFT calculated spectrum gives three absorptions at 416, 505, and 628 nm, of which the blue-shifted absorption is of very low intensity. A similar weak absorption at 405 nm is observed in the experimental spectrum. The calculated strong absorption at 505 nm and the weak absorption at 628 nm are interpreted to jointly correlate with the observed broad absorption at 552 nm (see Table 1). Additional weak absorptions are predicted by the TD-DFT calculations at 1051 nm for $[6a]^−$ and 889 nm for $[6a]^{2−}$, but these are not observed in the experimental spectra (probably due to their weakness and broadening). The TD-DFT calculations do not reproduce the experimental electronic spectra very precisely, and some deviations in the range between 400 and 700 nm are apparent. The calculated band at 423 nm for $[6a]^−$ is predicted at an overly high energy (experimental 508 nm), while for $[6a]^{2−}$ the predicted energy separation between the two calculated bands at 628 and 505 nm is larger than that observed (one broad peak at 508 nm). Nonetheless, overall the calculations provide a useful guideline to assign the bands.

**Chemical Reduction of the Dibenzo(phosphine**

With Elemental Sodium. Encouraged by the CV and UV−vis spectroelectrochemical results, we set out to synthesize and isolate the singly (1e) and hopefully the doubly (2e) reduced dibenzo[bf]phosphine. On the basis of the CV data we chose elemental sodium as a reducing agent ($E^0$(Na) = −3.04 V vs Fc/Fc⁺). When 10 equiv was added at room temperature to a solution of 6a in THF, the initial yellow mixture turned deeply purple over 4 h. The EPR spectrum confirmed that the

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**Figure 3.** Cyclic voltammograms of 6a: full (blue) and separate (red) scans over the first reduction wave and full (green) scan over the second one. Scan rate: 200 mV s⁻¹. Signals marked with * stem from the irreversible oxidation at potentials > +0.55 V. Signals marked with # are attributed to a reaction product of $[6a]^{2−}$ with traces of water (see text).

**Scheme 4. One- and Two-Electron Reduction of Dibenzo[bf]phosphepine 6**

![Scheme 4](image-url)
radical anion Na'[6a]− had formed (Figure 5a, Scheme 4); the solution was NMR silent.

A satisfactory EPR spectrum could be simulated with parameters that reflect delocalization of the spin density over the olefinic and aromatic carbons (Table 2, Figure 5). Resolved hyperfine couplings with 13 nuclei in 7 independent sets were obtained: i.e., with the phosphorus atom, the olefinic hydrogens (H1), four sets of aromatic hydrogen nuclei (H2–5), and a small, poorly resolved coupling with the meta hydrogens (H7) of the phenyl substituent (Figure 5a). The assignment of the hyperfine couplings is based on supporting DFT calculations (ORCA, B3LYP/TZVP,19 geometry optimized with Turbomole at the BP86/SV(P) level21) of Na'[6a]− (Table 2, Supporting Information). Evidently, reducing 6a to [6a]− places an electron in the fully delocalized π* SOMO with a similarly shaped spin density distribution (Figure 6) in support of the observed EPR spectrum.

The EPR spectrum for the mesityl-derivative Na+[6b]− was obtained likewise (Figure 5b), but it is broader than that of Na'[6a]− even at low concentrations. Consequently, the

Table 1. TD-DFT Parameters of the UV−Vis Spectra of [6a]− and [6a]2−

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<td>416</td>
<td>10</td>
<td>HOMO → LUMO+10</td>
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αOrca, TD-DFT, B3LYP/def2-TZVP, COSMO ε = 2.28.

Figure 5. Experimental (in THF) and simulated EPR spectra of (a) Na+[6a]− (frequency 9.357723 GHz; microwave power 2 mW; T = 298 K; modulation amplitude 1 G) and (b) Na+[6b]− (frequency 9.359971 GHz; microwave power 2 mW; T = 298 K; modulation amplitude 0.2 G). (c) Atom numbering used for the hyperfine couplings in Table 2.

Table 2. Experimental and DFT g Values and Hyperfine Couplings (MHz) of Na+[6a]− and Na+[6b]−

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</tr>
<tr>
<td>H7,d</td>
<td>−0.36</td>
<td>−0.54</td>
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αDerived from least-squares curve fitting of the spectrum recorded in THF at T = 298 K. The signs were assigned on the basis of the DFT calculations. βB3LYP/TZVP. γSee Figure 5 for atom numbering. δTwo equivalent hydrogens. ϵPoorly resolved.
smallest hyperfine couplings with the HS hydrogens are poorly resolved and those with the H7 hydrogens of the P-Mes group are not resolved at all (Figure 5b, Table 2). The spectrum could be simulated in a satisfactory manner using the DFT-calculated values for [6b\(^{+}\)]\(^{-}\) as a starting point (Table 2, Supporting Information). The DFT optimized structures of the two radical anions adopt the same conformations as their neutral precursors, that is I for [6a\(^{-}\)]\(^{-}\) and II for [6b\(^{+}\)]\(^{-}\) (Figure 2), but with longer C7–C8 double (1.39–1.40 Å vs 1.35 Å) and shorter C6–C8 single bonds (1.42 vs 1.46 Å) for the seven-membered ring, reflecting its delocalized nature (see Figure 1 for numbering).

Single crystals suitable for X-ray diffraction were obtained by slow vapor diffusion of pentane into the THF solution obtained from the reaction of 6a with sodium. Surprisingly, these proved to be of dianionic [Na\(^{+}\)]\([\text{6a}^{-}]\) (Figure 7) instead of the expected radical anion [Na\(^{+}\)]\([\text{6a}^{-}]\), which was observed by EPR spectroscopy. Dianion 6a\(^{2-}\) crystallizes as a dimer with two [6a\(^{2-}\)]\(^{-}\) species bridged by three THF molecules ([Na\(^{+}\)]\([\text{6a}^{-}]\); THF) (Figure 7). Apparently, the purple solution that is obtained by mixing 6a with 10 equiv of metallic sodium consists of a mixture containing both the singly and doubly reduced products [Na\(^{+}\)]\([\text{6a}^{-}]\) and [Na\(^{+}\)]\([\text{6a}^{-}]\).

The molecular structure of the dianion adopts conformation I just like the neutral precursor, but charge delocalization profoundly affects the C–C bonds, lengthening the “aromatic” C1–C6 ([6a\(^{2-}\)]\(^{-}\) 1.462(3) Å vs 6a 1.4089(18) Å) and C7–C8 “double” bonds ([6a\(^{2-}\)]\(^{-}\) 1.462(3) Å vs 6a 1.338(2) Å) and shortening the C6–C7 “single” bonds ([6a\(^{2-}\)]\(^{-}\) 1.396(3) Å vs 6a 1.4669(19) Å), while the P-pyramidality remains essentially unchanged (sum of the bond angles around phosphorus: [6a\(^{2-}\)]\(^{-}\) 310.81(14)° vs 6a 308.96(10)°).

Magnetic susceptibility measurements at room temperature on crystals of [6a\(^{2-}\)]\(^{-}\) (\(\mu_{eff} \approx 0\)) show a closed-shell configuration, which is favored by 14.9 kcal mol\(^{-1}\) over the triplet excited state according to B3LYP/6-311G(d,p) calculations. Nonetheless, no \(^{31}\)P NMR spectrum of dianionic [6a\(^{2-}\)]\(^{-}\) could be recorded, likely due to the presence of (trace amounts of) the radical anion, as rapid electron transfer between the two species is expected to cause substantial NMR signal broadening.

Two mechanistic pathways can lead to formation of dianion [6a\(^{2-}\)]. First, reduction of [6a\(^{+}\)]\(^{-}\) with excess sodium may occur. The redox potential corresponding to the second reduction of 6a (\(E_{1/2} = −3.03\) V vs Fc/Fc\(^{+}\)) is very close to the reduction potential of sodium (\(E^* = −3.03\) V vs Fc/Fc\(^{+}\)), which does in fact explain the presence of both [6a\(^{2-}\)]\(^{-}\) and [6a\(^{3-}\)]\(^{-}\) in the reaction mixture.\(^{\text{2b}}\) Second, disproportionation (2[6a\(^{+}\)]\(^{-}\) \(\Leftrightarrow\) [6a\(^{2-}\)]\(^{-}\) + 6a) may be followed by selective crystallization of [Na\(^{+}\)]\([\text{6a}^{-}]\). On the basis of the CV redox potentials, this disproportionation equilibrium lies strongly to the left (\(\Delta G^\circ = 9.4\) kcal mol\(^{-1}\)), but crystallization of [6a\(^{2-}\)]\(^{-}\) may be feasible given the equilibrium constant of \(K_{\text{disp}} \approx 1 \times 10^{-7}\).

Unfortunately, we were unable to grow crystals of [Na\(^{+}\)]\([\text{6b}^{-}]\)\(^{2-}\), possibly due to its higher solubility. However, like its neutral precursor, B3PW91/6-311G(d,p) calculations show a preference for conformation II and, like [6a\(^{2-}\)], elongated “aromatic” and “double” C–C bonds (\(d_{\text{C7–C8}} = 1.35\) Å (6b\(^{+}\)), 1.42 Å ([6b\(^{2-}\)]\(^{-}\)); \(d_{\text{C1–C6}} = 1.41\) Å (6b\(^{+}\)), 1.46 Å ([6b\(^{2-}\)]\(^{-}\)) and shortened “single” bonds (\(d_{\text{C8–C7}} = 1.46\) (6b\(^{+}\)), 1.40 Å ([6b\(^{2-}\)]\(^{-}\))) for the phosphine ring. In summary, the collective UV–vis, structural, and computational data show that upon 1e reduction an electron is placed in the \(\pi^*\) LUMO of 6, being the SOMO of [6\(^{+}\)]\(^{-}\), and two on 2e reduction, forming the HOMO of [6\(^{2-}\)]\(^{-}\) without changing the conformation, which is I for the P-phenyl and II for the P-mesityl derivative (Figures 6 and Figures S6 and S8 (Supporting Information)). Electronically, the dibenzo[b\(fi\)]-phosphine rings in [6\(^{+}\)]\(^{-}\} and [6\(^{2-}\)]\(^{-}\}] are then best viewed as a combination of two isolated fragments, namely a 1e- or 2e-reduced \(\pi\)-conjugated stilbene base and a noninteracting phosphane lone pair, making them ideal ligands for coordination chemistry.

**Complexation to Rhodium(I).** To probe the ability of 6a and 6b to act as heterobidentate phosphate–olefin ligands, we investigated their affinity for Rh\(^{3+}\) precursors as a necessary first step toward exploring their “redox noninnocence” features and behavior in catalysis. First, we show that both are potent chelating ligands, despite their conformational differences.

We start with the coordination chemistry of ligand 6a. Despite the fact that the phosphorus lone pair and the olefinic double bond of the free ligand are not preorganized for metal chelation (Figure 2), pyramidal inversion at P1 occurs readily, allowing the ligand to act as a heterobidentate phosphate–
olefin ligand. The reaction of 6a with $[\text{Rh(cod)}_2][\text{OTf}]$ in a 3:1 ratio in DCM (room temperature, 16 h) led to the quantitative formation of the yellow-coordinate-complex 8a (Scheme 5). A lower ligand: Rh ratio (2:1) also leads to formation of 8a (based on $^{31}$P NMR), but with incomplete conversion of the Rh$^{1}$ precursor.

**Scheme 5. Coordination of 6a with Rh$^{1}$ Species**

The molecular structure of 8a, resolved by X-ray crystal structure determination (Figure 8), reveals a strongly distorted trigonal bipyramidal complex ($r = 0.61$) carrying two heterobidentate benzophosphene ligands with axial phosphorus atoms and equatorial double bonds and a third (equatorial) benzophosphene that coordinates to the rhodium by its phosphorus atom only. This Rh–P3 bond is longer than the other Rh–P1 and Rh–P2 bonds (2.4232(11) vs 2.2973(11) Å), which points to substantial π-back bonding between the olefinic bonds (1.422(6)–1.432(6) vs 1.334(6) Å), which points to substantial π-back bonding and hence a strong metallo-cyclopropene resonance contribution. Remarkably, complex 8a adopts conformations II and III for the bidentate ligand and II for the monodentate ligand, in contrast to the preferred conformation I for the free ligand (Figure 2). This may be of steric origin, although chelating effects may also contribute.

The room-temperature $^{31}$P NMR spectrum of 8a shows a sharp doublet of triplets ($J_{\text{PRh}} = 119.0, J_{\text{PP}} = 29.5$ Hz) at 20.5 ppm and a very broad signal at 36.0 ppm (Figure 9a). Lowering the temperature leads to sharpening of the low-field signal to three doublet of doublets of doublets at 215 K ($^{31}$P NMR 19.7 ppm ($J_{\text{PRh}} = 119.0, J_{\text{PP}} = 38.1, J_{\text{PP}} = 21.8$ Hz), 31.4 ppm ($J_{\text{PRh}} = 395.0, J_{\text{PP}} = 95.2, J_{\text{PP}} = 21.8$ Hz), 39.2 ppm ($J_{\text{PRh}} = 395.0, J_{\text{PP}} = 95.2, J_{\text{PP}} = 38.1$ Hz) (Figure 9e). The signals at 39.2 and 31.4 ppm show a very large trans $J_{\text{PP}}$ coupling constant of 395.0 Hz and are therefore assigned to stem from the two trans-positioned phosphorus atoms in the bipyramid.

VT-$^{31}$P NMR (Figure 9) reveals a dynamic process due to Rh–P3 bond rotation of the monodentate ligand in 8a (Scheme 6). The magnetic anisotropy of the aryl rings of this ligand affects the chemical shifts of the two trans-positioned axial phosphorus atoms, which explains their inequivalence (39.2 and 31.4 ppm) below the coalescence temperature and their dynamic interconversion above. Rotation of the monodentate ligand does not affect its own chemical shift in the 215–298 K temperature range but averages the $J_{\text{PP}}$ couplings with the axial P atoms ($J_{\text{PP}} = 38.1$ and 21.8 Hz) to $J_{\text{PP}} = 29.5$ Hz at the coalescence temperature, where these atoms become equivalent on the NMR time scale. The experimental $\Delta G^\circ$ value for Rh–P3 bond rotation of the equatorial ligand is estimated at 12.6 kcal mol$^{-1}$.23

In sharp contrast to the Rh$^{1}$ coordination of 6a, the analogous reaction with 6b yielded (91%) by $^{31}$P NMR a 10:1 mixture of the square-planar $[\text{Rh}(6b)_2][\text{OTf}]$ complexes cis-8b ($\delta^{(31)}(34.6$ ppm) and trans-8b ($\delta^{(31)}(43.1$ ppm) in DCM ($\delta^{(31)}(3.5$ ppm) below the coalescence temperature and which carry two instead of three ligands (Scheme 7). It is noteworthy that 8b, in contrast to 8a, does not reveal any dynamic behavior on the NMR time scale. Deep red crystals of the major isomer cis-8b were obtained in 55% yield by slow evaporation of pentane into the dichloromethane solution of the mixture. The molecular structure of 8b (Figure 10) reveals a cis coordination mode for the two dibenzophosphine rings. In the crystal structure we find an intramolecular π-stacking interaction between the two mesityl substituents. These substituents are nearly parallel (deviation 2.62°), and the centers of the rings have perpendicular distances to the neighboring ring plane of 3.5945(9) and 3.5807(11) Å, respectively. This interaction may explain the relative stability of cis-8b over the trans-8b isomer. Dibenzophosphine in cis-8b adopts conformation III, which is higher in energy than conformation II for the free ligand. Coordination of this higher energy conformation is perhaps less surprising than is the case for 8a. Obviously, II would lead to substantial steric repulsion between two mesityl rings in cis-8b.

The phosphorus atoms of 8b (320.74(16)° for P1 and 320.14(17)° for P2) are slightly less pyramidal than in 6b (312.21(15)°) and diaminon (6a)° according to the sums of their bond angles. The P–Rh bonds have lengths similar to the equatorial bonds of 8a (2.2823(5)–2.3079(5) Å) and 2.2973(11)–2.3567(11) Å, which are higher than in the cis-8b system. The C7–C8 double bonds are likewise elongated compared to those of the free ligand (1.400(3)–1.405(3) vs 1.332(3)–1.339(3) Å), indicating substantial metal-to-ligand π-back-bonding. The observed difference in the ligand to Rh coordination stoichiometry between 8a (3:1) and 8b (2:1) is presumably caused by the steric crowding of the methyl groups in 6b. Complex cis-8b[OTf] is sparsely soluble in ethers, which hampers a study of its redox properties. To increase the solubility in THF, we exchanged the triflate ion by stirring cis-8b[OTf] with NaBArF (BArF$^-$ = $B(C_6H_4(CF_3)2)_2^{-}$) in DCM to obtain deep red crystalline cis-8b[BArF]$^-$ (80%). Its cyclic
voltammogram (Figure 11) shows two cathodic waves with $E_{1/2} = -1.45$ and $-1.80 \text{ V (vs Fc/Fc')}$. The first corresponds to a reversible one-electron reduction ($I_f/I_b = 1.0$) and the second to a nonfully reversible two-electron transfer ($I_f/I_b \approx 1.3$). Unfortunately, the closeness of these potentials and the unpreventable disproportionation hamper the isolation of the rhodium(0) radical anion, which agrees with our inability to isolate reduced species from the reaction of $8b$[$\text{BArF}$] with either sodium or cobaltocene as reducing agent. Cyclic voltammetry of $8a$ (see Supporting Information, Figure S3) revealed one reversible cathodic wave at $-1.71 \text{ V}$ and several nonreversible waves at lower potentials.

**CONCLUSIONS**

In this paper we describe the synthesis, redox properties, and initial coordination studies of new heterobidentate phosphane–olefin ligands based on the dibenzophosphapine scaffold. The $P$-phenyl and $P$-mesityl derivatives $6a,b$ are readily synthesizable from commercially available precursors. They show interesting redox activity as free ligands and can be reduced by sodium to the radical anion [$6a^*$]$^-$ and dianion [$6a^2$]$^2$,

which are electronically best described as a combination of two isolated fragments, that is a 1e (or 2e) reduced stilbene fragment and a phosphane lone pair. Dibenzophosphapines deserve attention as new heterobidentate phosphane–olefin ligands in the coordination chemistry to late transition metals, as demonstrated for Rh. The structure of the rhodium complexes can be tuned by changing the substituents at the phosphorus atom. Thus, whereas dibenzophenyl phosphapine $6a$ gives the 3:1 (ligand:Rh) complex $8a$, the more bulky mesityl analogue $6b$ leads to the 2:1 complex $8b$. In the distorted-trigonal-bipyramidal $8a$ two of the dibenzophosphapines act as bidentate ligands, while the third ligand binds as a monodentate $P$ donor. In the square-planar complex $cis-8b$ both dibenzophosphapine ligands $6b$ coordinate in a bidentate fashion. Interestingly, the ligands in these two complexes adopt conformations that are less favorable for the noncoordinated
dibenzo(18-crown-6)phosphines. These initial investigations on the dibenzo(18-crown-6)phosphine ligand system bode well for the future, where we will explore their "redox noninnocent" behavior and their potential to generate new classes of transition-metal-based catalysts.

**EXPERIMENTAL SECTION**

**General Considerations.** All syntheses were performed with the use of Schlenk techniques under an atmosphere of dry nitrogen. Pentane, THF, toluene, and diethyl ether were distilled under nitrogen from calcium hydride. Bu₄NPF₆ was dried under vacuum.

**NMR: Bruker Advance 250 (235 MHz) using BF₃·OEt2 as an external standard (δ 0.0 ppm). All NMR signals are given in ppm.**

**Synthetic Procedures. 5-Phenyl-5H-dibenzo[bf]j]phosphapenta- Borane (7a).** A solution of (Z)-1,2-bis(2-bromophenyl)ethene (5, 1.83 mmol, 618 mg) in 9 mL of diethyl ether was added dropwise to a solution of t-BuLi (7.32 mmol, 4.58 mL of 1.6 M solution in pentane) in 9 mL of diethyl ether at −78 °C, and the mixture was stirred for 1.5 h at this temperature. Then, phenyldichlorophosphine (1.83 mmol, 328 mg, 0.25 mL) was added, and the reaction mixture was warmed to room temperature. After the mixture was stirred at room temperature for 1.5 h, a 2.0 M solution of BH₃·SMe₂. If conversion is not completed, more BH₃·SMe₂ solution should be added.Mp: 182–184 °C (colorless crystals).

1H NMR (400 MHz, CDCl₃): 1.35 (q, JHH = 7.9, JHP = 7.5 Hz, CH₃), 6.81 (s, 2H, H-1), 6.90–6.92 (m, 2H, o-C₆H₅), 7.18 (td, 2H, JHH = 7.5, JHP = 2.3 Hz, m-C₆H₅), 7.30 (m, 1H, p-C₆H₅), 7.46–7.49 (m, 2H, H-2), 7.59–7.64 (m, 4H, H-3, H-5), 8.42–8.47 (m, 2H, H-4).

31P [1H] NMR (162 MHz, CDCl₃): 13.4 (δpp = 71.8 Hz).

Cyclic voltammetry of cis-8b [BARF]. Scan rate: 100 mV s⁻¹.

Experimental X-band EPR spectra were recorded on a Bruker EMX spectrometer. The spectra were simulated by iteration of the anisotropic g values, (super)hyperfine coupling constants, and line widths using the W95EPR program (available upon request from Prof. Frank Neese, Max Planck Institute for Biorganic Chemistry).

Flash chromatography: silica gel SiliaFlash P60 (0.040–0.063 mm) with an overpressure of about 0.5 bar. Melting points were determined on samples in unsealed capillaries on a Stuart Scientific SMP3 melting point apparatus and are uncorrected. (Z)-1,2-Bis(2-bromophenyl)ethene (5) and mestyledichlorophosphate (6) were prepared according to the literature procedures.

**DFT Calculations. DFT Conformational Analysis.** The conformational analysis of [6a] and [6b]⁺, as well as the spin state energies of [6a]⁺, were evaluated with Gaussian03 at the B3PW91 level of theory. In this functional, the exchange energy is described with contributions from local and nonlocal (B3-parameter Becke29 and Hartree–Fock (HF)) exchange terms, and the correlation energy is given by the Perdew and Wang 91 nonlocal functional within the generalized gradient approximation (GGA). The 6-311G(d,p) basis set for atoms C, H, N, O, and P has been used. The nature of each stationary point was confirmed by a frequency calculation. Relative energies were corrected with zero-point energies.

**DFT Property Calculations.** The geometries of the full atom models of [6a]⁺ and [6a]⁺⁺ were optimized with the Turbomole program coupled to the PQS Baker optimizer at the B3PW91 DFT level. The EPR parameters of [6a]⁺ and [6b]⁺⁺ were subsequently calculated with ORCA, using the B3LYP functional and TZ2P basis set employing COSMO dielectric solvent corrections (ε = 2.28). The coordinates from the structure optimized in Turbomole were used as inputs for the ORCA calculations. Orbital and spin density plots were generated with Molden.38
5-Phenyl-5H-dibenzo[b,f]phosphepine (6a). A 1.14 g portion (10.2 mmol) of DABCO was added to a solution of 1.53 g (5.1 mmol) of 7a in 40 mL of toluene at room temperature, and the mixture was stirred overnight. The next day the mixture was quenched with a 5% aqueous solution of HCl and extracted with diethyl ether. The combined organic extracts were dried with MgSO₄ and all volatiles were removed under reduced pressure. This gave 1.42 g (4.97 mmol, 97%) of phosphepine 6a as a colorless solid. It is recommended to monitor the reaction by ³¹P NMR before isolation, since in some cases we observed slow deborylation of the BH₃ adduct. If conversion is not completed, more DABCO should be added. Mp: 132–134 °C (colorless solid).

³¹P NMR (500 MHz, CDCl₃): 6.78 (s, 2H, H-1), 6.90 (dd, 2H, J₉H = 7.7, J₁₀H = 1.7 Hz, m-pH), 7.13–7.20 (m, 7H, o-C₆H₅−P). 31F{¹H} NMR (162 MHz, CDCl₃): –81.1. ¹³C{¹H} NMR (126 MHz, CDCl₃): 127.4 (p-P), 127.7 (d, JCP = 4.8 Hz, o-P), 128.2 (d, JCP = 15.2, C-5S), 129.7 (d, JCP = 0.7 Hz, C-3), 130.5 (d, JCP = 1.6 Hz, C-2), 131.4 (d, JCP = 16.3 Hz, m-pH), 132.6 (d, JCP = 13 Hz, C-1), 135.8 (d, JCP = 9.3 Hz, C-Su), 137.0 (d, JCP = 45.8 Hz, C-S/4), 137.4 (d, JCP = 9.5 Hz, Ph-P), 139.9 (C-1u). δ: 33048 (m), 3009 (m), 1476 (m), 1427 (m), 1264 (m), 804 (s), 775 (s), 740 (s), 694 (s), 496 (m), 460 (m). HR-ESI-MS: calcd for C₂₃H₂₃BP [M + H]⁺: 327.0507, found 327.0579; m/z (%) 97 (100), 119 (100), 141 (100), 163 (100), 185 (100). ³¹P[H] NMR (162 MHz, CDCl₃): –30.5, ¹¹B[H] NMR (101 MHz): 21.4 (p-CH₃,Mes), 24.6 (d, JPB = 18.9 Hz, o-CH₃,Mes), 125.5 (d, JCP = 84.7 Hz), 127.4, 128.5, 129.7 (d, JCP = 6.3 Hz), 129.8 (d, JCP = 4.7 Hz), 130.4 (d, JCP = 4.7 Hz, C-S), 137.8 (d, JCP = 16.5 Hz), 138.6 (d, JCP = 21.0 Hz), 140.6 (d, JCP = 1.4 Hz), 147.0 (d, JCP = 17.2). δ: 36051 (w), 3012 (w), 2963 (w), 2917 (w), 2853 (w), 1469 (m), 1423 (m), 1094 (m), 1027 (m), 800 (s), 747 (s). HR-FAB MS: for C₂₃H₂₃BP(N + H): 329.1459, found 329.1459; m/z (%) 97 (100), 119 (100), 141 (100), 163 (100), 185 (100). Reduction of 5-Mesityl-5H-dibenzo[b,f]phosphepine (6b) with Sodium. Sodium was added to a solution of phosphepine 6a in THF and 115 mg (5.0 mmol) of sodium was added to this solution at room temperature. Upon stirring, the reaction mixture changed color from red to deep purple. After 4 h of stirring at room temperature the solution was decanted from unreacted sodium. The mixture was ³¹P NMR silent. Crystals of the diastereomeric base 6a (96%) were obtained by slow evaporation of pentane into the THF solution obtained after decantation from sodium; these were also ³¹P NMR silent.

5-Mesityl-5H-dibenzo[b,f]phosphepine–Borane (7b). A solution of (Z)-1,2-bis(2-bromophenyl)ethene (5g) 4.70 mmol, 1.59 g) in 30 mL of diethyl ether was added dropwise to a solution of nBuLi (18.82 mmol, 11.7 mL of a 1.7 M solution in pentane) in 30 mL of diethyl ether at −78 °C, and the mixture was stirred for 1 h at this temperature. Then, metystyldichlorophosphine (18% mixture of MesPCl₃ and MesPClBr, approximately 4/1, 4.70 mmol, 1.08 g) in 15 mL of diethyl ether was added, and the reaction mixture was warmed to room temperature. The mixture was stirred at room temperature for 1 h. Full conversion was observed with ³¹P NMR. After that a 2.0 M solution of BH₃⋅SMe₂ in diethyl ether (4.94 mmol, 2.47 mL) was added dropwise to the reaction mixture at room temperature. The mixture was stirred overnight, followed by the addition of water (20 mL) and diethyl ether (40 mL), filtration through Celite, and column chromatography purification on silica (MTBE/pentane 10/1, then 10/1). This gave 520 mg (1.52 mmol, 32% yield) of 7b as a colorless solid. It is recommended to monitor the reaction by ³¹P NMR before isolation, since in some cases we observed slow formation of the BH₃ adduct (this, probably, depends on the quality of BH₃⋅SMe₂). If conversion is not completed, more BH₃⋅SMe₂ solution should be added.

³¹P NMR (500 MHz, CDCl₃): 1.43 (q, JPH = 79.5 Hz, BH₃), 1.55 (s, 6H, o-CH₃,Mes), 2.19 (s, 3H, p-CH₃,Mes), 6.63 (d, 2H, JHP = 2.8 Hz, m-pH), 6.85 (s, 2H, H-1), 7.38 (2H, JHP = 6.9 Hz, H-2), 7.48–7.57 (m, 4H, H-3, H-4, H-5). ³¹P[H] NMR (162 MHz, CDCl₃): 10.4 (q, JPH = 74.1 Hz). ¹¹B NMR (128 MHz, CDCl₃): –39.8 (m). ¹³C[H] NMR (101 MHz, CDCl₃): 20.9 (s, p-CH₃,Mes), 22.8 (d, JCP = 5.5 Hz, o-CH₃,Mes), 121.5 (d, JCP = 57.2 Hz, p-Mes), 128.7 (d, JCP = 66.8 Hz, C-2), 129.2 (d, JCP = 130.3 Hz, C-4), 130.5 (d, JCP = 56.1 Hz, C-Sa), 130.68 (C-3), 130.73 (d, JCP = 65.9 Hz, m-Mes), 131.7 (d, JCP = 1.7 Hz, C-1), 133.1 (d, JCP = 18.1 Hz, C-S), 138.4 (C-1a), 139.7 (d, JCP = 2.6 Hz, p-Mes), 142.0 (d, JCP = 8.5 Hz, o-Mes). δ: 30588 (w), 2970 (w), 2970 (w), 2328 (s), 2343 (m), 1451 (m), 1136 (w), 1058 (s), 804 (s), 775 (m), 743 (m), 460 (m). HR-
Organometallics

19F{1H} NMR (235 MHz, CD2Cl2) −78.7; 13C{1H} NMR (101 MHz, CDCl3) 21.2 (p-CH(Me), 27.3 (p-CH(Me)), 96.6 (C-1), 113.9 (d, JCP = 44.1 Hz, i-Mes), 121.5 (q, JCP = 318.8 Hz, CF3), 127.1 (C-3/4/5), 127.5 (C-7 = 70.0 Hz, C-2), 129.6 (C-3/4/5), 129.9 (C-3/4/5), 131.4 (t, JCP ≈ JCP = 3.9 Hz, m-Mes), 134.9 (d, JCP = 43.1 Hz, C-5a/1a), 142.0 (p-Mes), 142.5 (p-Mes), 144.2 (d, JCP = 22.6 Hz, C-1a/5a). IR: ν 3058 (w), 2966 (w), 2920 (w), 1455 (m), 1260 (s), 1154 (m), 1030 (s), 677 (s). HR-FAB MS: calcld for C46H42P2Rh (M−200) 759.1817, found 759.1828; 11B NMR (128 MHz, CDCl3): 20.7 (s), 67.4 (s, 4H), 7.15−7.20 (m, 4H), 7.25−7.32 (m, 8H), 7.44−7.49 (m, 1H), 7.90 (s, 4H), 7.77 (s, 7H). 31P{1H} NMR (126 MHz, CDCl3): 33.3 (d, JPP = 142.8 Hz). 18B NMR (128 MHz, CDCl3): −6.6 (s). 19F{1H} NMR (235 MHz, CDCl3): −62.8. 13C{1H} NMR (126 MHz, CDCl3): 20.7 (p-CH(Me)), 26.9 (o-CH3(Me)), 95.7, 113.0, 117.4, 124.6 (q, JCP = 278.4 Hz, CF3), 126.8, 126.9, 128.9 (q, JCP = 30.8 Hz, C−C), 129.3, 129.8, 131.1, 134.4, 141.9, 142.2, 143.4 (d, J = 20.3 Hz), 162.2 (q, JCP = 49.7 Hz, C−B). IR: ν 3072 (w), 2927 (w), 1610 (w), 1455 (s), 1352 (m), 1278 (s), 1126 (s), 881 (w). HR-FAB MS: calcld for C46H42P2Rh (M−200) 759.1817, found 759.1828; 13C{1H} NMR 759 (100) [M−OTf], 431 (50) [M−OTf−6Bh], 310 (12), 251 (6), 178 (4).

ASSOCIATED CONTENT

Supporting Information

Text, figures, tables, and CIF files giving experimental synthetic procedures, Cartesian coordinates and energies of all stationary points (DFT), crystallographic data, NMR spectra of all new compounds, EPR spectra of the compounds [6a]5− and [6b]5−, and cyclic voltammograms of 6a, 8a, and 6b. This material is available free of charge via the Internet at http://pubs.acs.org.

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Notes

The authors declare no competing financial interest.

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REFERENCES


(23) Calculated from the simplified Eyring equation $\Delta G^\ddagger = (4.575 \times 10^{-10}) T \left[ \frac{9972 + \log(T/\Delta S)}{T} \right]$ (kcal mol$^{-1}$), where $T_s$ is the coalescence temperature (in K), $T_c = 298$ K for 8a and $\Delta S$ is the difference in chemical shifts (Hz) at 215 K.


(25) For the disproportionation equilibrium $2\text{[8b]}^2+ \rightleftharpoons \text{[8b]}'^2+ + 8b$, $\Delta G^\ddagger = 33.8$ kcal mol$^{-1}$ and $K_{\text{disp}} \approx 1 \times 10^{15}$.


